Learning Objectives

• Understand the spatial and temporal diversity of toxicological and contamination events.
• Describe the linkage between natural forces and chemodynamics of contaminants.
• List important zones of impact and understand the relationships of human activity and potential for chemical release and contamination.

Learning Objectives, 2

• Understand the relationship of transport and specific chemical processes of contaminants.
• Explore, as an example, the fundamental processes of dissimilatory iron reducing bacteria and their role in contaminant transformation and transport.
• Develop knowledge of groundwater movement and processes related to contamination.

Learning Objectives, 3

• Understand the interaction of non-aqueous phase liquids with groundwater.
• Gain an introductory understanding of atmospheric transport of contamination using acid rain as an example.

Transport of Contaminants

• Spatial and temporal diversity.
  – Impact can be local to global.
  – Timescale of interest can be seconds to millennia (radionuclides).
• Important interactions between molecular events and biological events.
  – Beyond even the population level.
• Important interactions between chemodynamics (e.g., fugacity, volatilization, dissolution) and the forces of nature.
  – Wind (thermal), water (thermal, gravity), biological (movement, e.g., wings, fins).

Scale of Environmental Toxicology

- Ecosystem effects
- Community effects
- Population parameters
- Physiological and behavioral effects
- Biochemical and molecular effects
- Receptor and mode of action
- Biotransformation, sequestration
- Chemical and physicochemical characteristics
**Scale of Contamination**

- Small effects can have global implications.
  - All effects first at the molecular level.
- Chemodynamics and physical properties of the chemical interacting with the forces of nature define scale potential.
  - E.g., ozone depletion.
- Natural processes should not be ignored.
  - Chemical contributions, "evolutionary change"; early earth had a reducing atmosphere until photosynthesis contaminated the atmosphere with "toxic" oxygen.

**Natural Forces**

- Natural forces acting upon earth move mobile components of the ecosphere.
  - Atmosphere.
    - Gaseous and particulate transport.
  - Hydrosphere.
    - Surface water, ground water, atmospheric water.
  - Lithosphere.
    - Surface and subsurface soils, dust.
  - Biosphere.
    - Nutrient and contaminant cycling.

**Important Zones of Impact**

- Often interfacial, high population or diverse.
  - Coastal zones/waterfronts.
    - Historically popular place to discharge waste.
  - Estuaries.
    - Chemical changes at the fresh-salt water interface modify solution characteristics and reactivity of contaminants.
  - Riparian areas.
  - Wetlands.
    - Often closed or "confined" oasis populations.
  - Urban areas/nesting areas.
    - High population of receptors.

**Compartments**

- Intracompartment and interfacial chemodynamics will affect transport.
  - Rate of movement can impact if receptors are exposed and when.
    - Air → fast movement.
      - Can allow for few reactions between source and receptor.
    - Surface water → moderately fast.
      - Site specific considerations important.
    - Groundwater → slow.
      - Can allow for complex abiotic and biotic reaction pathways.

**Spatial and Temporal Scales**

Environmental Toxicology

- Landscape Dynamics
- Ecosystem Dynamics
- Populations, Population Dynamics
- Organismal Physiology, Behavior
- Microbial Proc. Also, Organ, Tissue Physiology

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Wetland Loss 1780-1980

Agricultural Chemicals

Toxic Releases to Land, 94

Hazardous Waste Generators

“Superfund” Sites, 1995

Nuclear Regulated Sites
Chemical Processes
- Transport is controlled by complex interactions between physical, chemical and biological processes.
- A mass balance equation to predict contaminant movement must also contain terms to account for chemical and microbiological processes.

Chemical Reactions
- Inorganic chemical reactions.
  - Solubility.
  - Dissolution.
  - Precipitation.
  - Complexation rxns.
  - Sorption and surface chemistry.
  - Ion exchange rxns.
  - Redox chemistry.
- Organic chemical reactions.
  - Sorption.
  - Hydrolysis.
  - Co-solvation.
  - Ionization.
  - Volatilization.
  - Dissolution.

Sorption
- Most important process affecting transport of organic contaminants.
  - For non-polar organics, sorption is considered a partitioning process between the aqueous phase and the porous medium.
  - Can be described by a linear Freundlich isotherm, where the sorbed concentration is a fn of aq concentration and the partition coefficient Kp.
- Mechanism of organic sorption is hydrophobic bonding between C and om.
### Co-Solvation and Ionization

- Processes that may decrease sorption and therefore increase transport.
- Co-solvation increases interaction of solute and solvent.
  - Important at the source since only large concentrations are effective.
- Acidic compounds (phenols/organic acids) can lose a proton and become more water soluble.

### Volatilization and Dissolution

- Important for volatile compounds.
- Volatilization determined by
  - Area (grain size, water content).
  - Vapor pressure.
- Rate of diffusion.
  - Solubility driven.

### Inorganic Chemicals

- Total concentration is less important because of speciation.
  - Not descriptive enough to determine properties.
- Knowledge of the speciation of a metal is required to predict transport.
  - Free ions.
  - Insoluble species.
  - Metal/ligand complexes.
  - Adsorbed species.
  - Immobilized by ion exchange.
  - Differing oxidation state.

### Solubility, Dissolution, Precipitation

- Mineral dissolution and weathering determine the natural composition of water.
  - Source of most of the inorganic ions.
  - Common ion effect.
- Natural weathering can modify pH.
- Leachate is a dissolution process.
- Precipitation happens when a solubility limit is reached.

### Complexation Reactions

- A metal ion reacts with an anion that functions as a ligand.
  - New soluble species called a complex.
- Transition metals form strong complexes
  - Fe(III) > Hg > Cu > Pb > Ni > Zn > Cd > Fe(II) > Mn > Ca > Mg
  - Ligands: OH⁻, Cl⁻, SO₄²⁻, CO₃⁻², S²⁻, F⁻, NH₃, PO₄³⁻, CN⁻
- Ligands usually in excess.
- Organic ligands: amines, phenols, humic materials.

### Ion Exchange Reactions

- "Sorption" to a three dimensional porous matrix containing fixed charges.
- Ions held by electrostatic forces rather than by coordination bonding.
- Anion binding to clays.
**Metal Oxide Surface Complexes**

- Outer-Sphere Complex
- Inner-Sphere Complex
- Surface Precipitate

**Redox Chemistry**

- Change of oxidation state.
- Important determinant for transport.
  - Cr (VI), toxic, mobile.
  - Cr(III), immobile, insoluble.
  - Se(VI), mobile, less toxic.
  - Se(IV), less mobile, more toxic.
- Redox state of an aquifer is closely related to microbial activity.
- Redox reactions that occur depend on the dominant electron potential.
  - The primary redox active species; e.g. Fe^{2+}/Fe^{3+}.

**Factors Affecting Mobility**

- Amount and form of the metal.
- Soil properties affecting metal retention.
  - Bulk density, surface area, particle size distribution, pH, redox status, ion exchange capacity, organic matter, metal oxides present, type and amount of clay minerals.
- Soil organic matter is one of the primary immobilizing processes for trace and toxic metals (subsoils lend greater mobility).
- Properties of the leachate phase.
  - Complexation w/ anions; Pb w/HCO3).

**Focus: Sedimentary Iron**

- Percent levels of iron oxides in soils and sediments can be a controlling factor in several abiotic and biotic pathways for fate and transport of organic and inorganic contaminants.

**Environmental Fe Reduction**

- Abiotic reduction by organics (e.g. reduced quinones, sulfhydryl groups).
- Abiotic reduction by inorganics (e.g. H_2S).
- Direct enzymatic activity of dissimilatory Fe(III)-reducing bacteria (FeRB).
  - Dissimilatory: not linked to uptake/assimilation.
  - Assimilatory: linked to uptake/assimilation.
**Coupled to Electron Transport**

**Dissimilatory Fe(III) Oxide Reduction**

- Fe(III) present as in natural highly insoluble oxide minerals at circumneutral pH.
- Fe(III) = solid-phase electron acceptor.
- Fe(III) oxide reduction requires direct contact between FeRB and oxide minerals.

**Coupled to Organic Matter Oxidation**

**Complex Organic Polymers**

- Hydrolysis
- Fermentation
- Organic Acids (e.g. acetate) + H₂
- Fe(III)-reducing bacteria (anaerobic respiration)
- CO₂ + Fe(II)

**Aquatic Sediment Iron**

**Iron Oxides**

- Distinct banding caused by precipitation of iron-oxides as a result of rise and falls in groundwater.
- Bands are highly reactive toward many contaminants and contain microorganisms whose ecology and function is linked to iron geochemistry.
Significance of DIOR

\[ \text{CH}_2\text{O} + 4\text{FeOOH} \rightarrow \text{HCO}_3^- + 4\text{Fe}^{2+} + 7\text{OH}^- \]

- Oxidation of natural organic matter.
- Suppression of other anaerobic respiratory processes (e.g., sulfate reduction, methanogenesis).
- Generation of high-iron groundwater.
- Alteration of pH/Alkalinity conditions.
- Generation of carbonate (siderite) and magnetic minerals (magnetite).

Significance of DIOR, 2

- Release of sorbed and/or coprecipitated trace/toxic metals & radionuclides during reductive oxide dissolution.

Fe\(\text{III}\)-Me\(^+\) + e\(^-\) \rightarrow Fe\(\text{III}\)-OH + Fe\(^{2+}\) + Me\(^{2+}\)

Fe\(\text{III}\)-(Me)OH + e\(^-\) \rightarrow Fe\(\text{III}\)-OH + Fe\(^{2+}\) + Me\(^{2+}\)

Significance of DIOR, 3

- Immobilization of trace/toxic metals, radionuclides during carbonate mineral precipitation (e.g., Sr).

\[ \text{FeOOH} + 2\text{HCO}_3^- + 2\text{Me}^{2+} + e^- \rightarrow \text{FeCO}_3(s) + \text{MeCO}_3(s) + \text{OH}^- + \text{H}_2\text{O} \]

\[ \text{FeOOH} + \text{HCO}_3^- + 2\text{Me}^{2+} + e^- \rightarrow \text{Fe(Me)}\text{CO}_3(s) + 3\text{OH}^- \]

Significance of DIOR, 4

- Fe\(^{II}\) (surface-bound) as a reductant for abiotic contaminant transformations.

\[ \text{R-NO}_2 \rightarrow \text{R-NH}_2 \]
\[ \text{CCl}_4 \rightarrow \text{CH}_x\text{Cl}_{4-x} + x\text{Cl}^- \]
\[ \text{Cr(VI)}(\text{aq}) \rightarrow \text{Cr(OH)}_3(s) \]
\[ \text{U(VI)}(\text{aq}) \rightarrow \text{UO}_2(s) \]
\[ \text{TcO}_4^-(\text{aq}) \rightarrow \text{TcO}_2(s) \]

Significance of DIOR, 5

- Production & maintenance of metal-reducing bacterial (MeRB) populations capable of reducing mobile toxic metals (e.g. Cr(VI), Co(III), U(VI)) to less mobile forms.

\[ \text{CH}_2\text{O} + \text{nutrients} + \text{FeOOH} \rightarrow \text{Fe}(\text{II}) + \text{HCO}_3^- + \text{MeRB} \]

\[ \text{CH}_2\text{O} + \text{U(VI)}(\text{aq}) + \text{MeRB} \rightarrow \text{UO}_2(s) + \text{HCO}_3^- \]

- Oxidation of aromatic hydrocarbons in petroleum-contaminated aquifers.

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Groundwater

- Half of US population use GW for drinking water.
- GW provides 1/5 of the fresh-water supply.
  - >30 trillion gallons of GW.
- Ground water can become surface water.
- Also serves as a sink for wastes (gravity!).
  - Accidental spills, fertilizer runoff, ag chemical leaching, leaky sewers, septic tank discharge, urban storm water runoff, industrial lagoons, waste injection wells.

Understanding Transport

- Prediction of time of arrival and concentration at a receptor monitoring well, water supply, surface water.
- Design of cost effective and safe waste management facilities.
- Installation of effective monitoring systems.
- Development of efficient and cost-effective strategies for remediation.

Contaminant Movement

- Contaminants in GW will move primarily in the horizontal direction that is determined by the hydraulic gradient.
- Contaminants will decrease in concentration because of dispersion (molecular and hydraulic), filtration, sorption, chemical processes and microbial degradation.
  - Some of these processes, such as dispersion, will treat all contaminants equally.
  - Prediction of movement is difficult because of the complexity of the subsurface.

Advection-Dispersion Theory

- Study of Advection/Dispersion is useful for predicting when an action limit will be reached.
  - Advection: transport of a non-reactive tracer at groundwater velocity.
  - Dispersion: molecular diffusion, hydrodynamic mixing; causes decrease in concentration with increase in length of flow.
- Need to understand A/D for risk assessment and remediation.

NAPL

- Non aqueous phase liquids.
- Non-soluble to slightly soluble.
- Description based on density of bulk contaminant relative to water.
- LNAPL.
  - Light non-aqueous phase liquids.
  - Floaters: petroleum hydrocarbons.
- DNAPL.
  - Dense non-aqueous phase liquids.
  - Sinkers: Chlorinated solvents; TCE.

Transport, Dissolution of NAPLS

- As NAPLs move through a soil column, they displace water and air.
- Water is the wetting agent so it tends to cover sand grains and line the pores.
  - NAPL goes around or through center pore.
- Since the phases are both active, the permeability of the geologic media changes.
  - Reduction in permeability depends on medium.
- Surfaces are “wetted” by H₂O.
Relative Permeability Example

- Cubic meter of soil with a 35% porosity and containing TCE at 20% residual saturation.
- Implies that there is 0.07 cubic meters of TCE (103 kg) within the soil.
- If the solubility of TCE is 1,100 mg/L and if groundwater flows through the soil at 1.7 cm/day, removal by dissolution will take 15.4 yrs!

LNAPLs

- As a spilled LNAPL enters the unsaturated zone, it flows through the central portion of the unsaturated pores.
- If the amount of product spilled is small, product flows until residual saturation is reached.
- A three phase system consisting of water, product, and air is formed.
- Partitioning can occur
  - Air, infiltrating H₂O.

LNAPLs - Large Volumes

- Product flows through the pore space to the top of the capillary fringe.
- Dissolved front and the LNAPL change the phase chemo and physical dynamics.
- Since it is lighter than water it tends to float on the capillary fringe → plume.
- Changes in the water table will effect the depth of the plume.
  - Remember residual saturation.
  - Can be “immobile” to H₂O once saturated.

DNAPLs

- Can have great mobility in the subsurface as a result of their relatively low solubility, high density and low viscosity.
- Do not readily mix with H₂O and therefore remain as separate phases.
- High density can drive DNAPLs deep into aquifers.
  - When a high density, low viscosity fluid meets a low density (relative), high viscosity fluid the flow is “unstable” and viscous fingering occurs.

DNAPL Dynamics

- In a spill, a DNAPL flows through the unsaturated zone by gravity towards WT.
- If only a small amount of DNAPL is spilled, it flows until reaching residual saturation in the vadose zone.
  - If there is water in the unsaturated zone, then DNAPL exhibits viscous fingering.
  - Without water, occasionally the DNAPL vapors can sink to the capillary fringe and contaminate the groundwater.

DNAPLs - Large Volumes

- DNAPL flows until it reaches the capillary fringe and begins to penetrate the aquifer.
- To do this the DNAPL must overcome the capillary forces between the water and the porous soil - critical height calculation.
  - E.g., perchloroethylene calculated critical heights can range from a few centimeters in coarse grains to tens of meters for clays.
- Unfractured clays can be effective DNAPL barriers.
Atmospheric Transport

- Local and distant impacts possible.
- Natural processes contribute.
- Requires:
  - Volatile chemical.
  - Dissolution in water vapor.
  - "Toxic fog" air buoyancy of particulates.

Example: Acid Rain

- Precipitation that is more acidic than "background" precipitation.
  - Scandinavia, Canada, US (1st observed in 1800s).
- Can deposit via wet deposition (e.g., rain, snow) or dry deposition (e.g., turbulent exchange, gravity).
  - Dry deposition is usually near an emission source.
- Wet deposition is spatially more distributed (≥10^2 km)
- Caused by S and N oxides.

pH of Rain

- Atmospheric carbon dioxide forms carbonic acid naturally in rainwater (pH = 5.6).
- "Normal" background considered to be pH 5-7.
- Ocean bacteria can produce sulfur dioxide and precipitation pH of 4.5.

Reaction of S, N Oxides

- A portion of S and N oxides released into the atmosphere are converted into sulfuric acid and nitric acid.
- More complex atmospheric reactions can occur (UV, ozone, hydroxyl radical).

Acid Rain Impacts

- Acid deposition impact is controlled by acidity of the precipitation, meteorological conditions, and buffering capacity of the receptor ecosystem.
- Aquatic systems.
  - Lake acidification in NE, fish loss due to low pH, high Al ion concentration, and low Ca.
- Forests.
  - Acidic cloud water is responsible for high elevation loss in some areas, as well as soil changes.

Acid Rain Impacts

- Agriculture.
  - Local deposition effects, but no known major spatially distributed impacts.
- Materials.
  - Steel corrosion; carbonate stone dissolution.
- Visibility.
  - Reduced visibility in eastern US due to sulfate aerosols.
- Human health.
  - Exposed populations = adverse health effects(?).